Topological insights in polynuclear Ni/Na coordination clusters derived from a schiff base ligand

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Topological insights in polynuclear Ni/Na Coordination Clusters derived from a Schiff base ligand

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Abstract

This article presents the syntheses, crystal structures, topological features and magnetic properties of two Ni^{II}/Na^{I} coordination clusters (CCs) formulated $[Ni^{II}_3Na(L1)_3(HL1)(MeOH)_2]$ (**1**) and $[Ni^{II}_6Na(L1)_5(CO_3)(MeO)(MeOH)_3(H_2O)_3]\cdot 4(MeOH)\ 2(H_2O)$ [**2** $4(MeOH)\ 2(H_2O)$] where H_2L1 is the semi rigid Schiff base ligand (E)-2-(2-hydroxy-3-methoxybenzylideneamino)-phenol). Compound **1** possesses a rare $Ni^{II}_3Na^{I}$ cubane (**3M4-1**) topology and compound **2** is the first example in polynuclear Ni/Na chemistry that exhibits a **2,3,4M7-1** topology.

Keywords

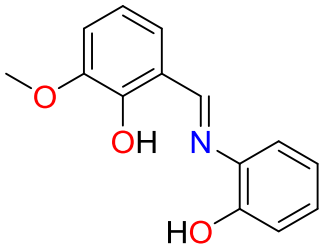
Coordination cluster, Nickel, Sodium, Topology, Schiff base, ferromagnetism, Carbonate ion

This work is dedicated to Prof Vladimir Ya. Shevcehnko on the occasion of his 75th birthday

1. Introduction and Review

One of the most complex categories of coordination compounds are polynuclear Coordination Clusters (CCs) that incorporate multiple metal ions into a single molecular entity and are linked by bridging ligands.[1] These entities are of great interest for their aesthetically beautiful structures,[2–4] unexpected transformations[5–7] and potential applications in magnetism,[8–10] luminescence,[11–15] catalysis,[16–18] etc. Paramagnetic transition metal CCs are of intense interest and have attracted a vast amount of attention since the discovery that some CCs behave as single molecule magnets (SMMs).[19–21] The Ni^{II} (d8) ion has second order orbital angular momentum, and zero-field splitting (ZFS) which can result in significant single-ion anisotropy and potentially in molecules exhibiting interesting magnetic properties.[22, 23] The interest in polynuclear Ni(II) coordination chemistry was first captured when the first Ni(II) based SMM, a Ni_{12} complex, was reported in 2001 by Cadiou et al.[24] Ever since, there have been a number of homometallic polynuclear Ni^{II} CCs with high nuclearities including, Ni_5,[7, 25] Ni_6,[26] Ni_7,[27, 28] Ni_8,[29–32] Ni_9,[33, 34] Ni_{11},[35] Ni_{12},[7] Ni_{13},[36] Ni_{14},[37] Ni_{20},[38] Ni_{21},[39] Ni_{24}.[40] and Ni_{26}[41] many of these display interesting magnetic properties including ferromagnetic, ferrimagnetic coupling, diamagnestism and SMM behaviour

Clusters of this size incorporate simple modified ligands with a wide variety of coordination modes for bridging; such as diethanolamine,[42] Schiff base,[43] carbide,[44, 45] and carboxylate.[46] The introduction of bridging groups can increase the nuclearity of a CC. Carbonate anions offer a diverse range of bridging modes within cluster type molecules, A number of high nuclearity CCs have been based on carbonate moieties[47, 48]. While Ni(II) CCs with bridging carbonate ligands are known, structural factors and magnetic exchange within these clusters greatly vary due to the large number of co-ordination modes of the CO_3^{2-} anion.[39, 49, 50]. Some interesting examples include; a Ni_6 containing a carbonato bridge[51] and an Ni_{12} where four Ni_4O_4 units are templated around a central CO_3^{2-} anion core.[52] On the other hand, the first reported mixed Ni^{II}/Na^{II} CC was reported in 1976 by Jonas for potential small molecule activation.[53] Since then a number of Ni^{II}/Na^{II} CCs have been reported, targeting for high nuclearity clusters and interesting magnetic properties; Ni_4Na_2,[54] Ni_4Na_5,[55] Ni_4Na_3,[56] Ni_4Na_4[57, 58] and others.[59–62] However since 2007 Ni^{II}/Na^{I} CCs with nuclearity over 10 have been reported far more frequently. The highest reported of these is a $Ni_{18}Na_6$ cluster[63] and the second $Ni_{16}Na_4$[64], both synthesised by calix[4]arene type ligands and the third is a $Ni_{16}Na_2$ cluster. In addition two $Ni_{12}Na_2$ clusters were reported by Christou et al.[37, 65] In all cases, similar anti-ferromagnetic behaviour was observed.



Scheme 1. The protonated form of the organic ligand H_2**L1** used in this study.

The diprotic Schiff base ligand (E)-2-(2-hydroxy-3-methoxybenzylideneamino)-phenol (H_2L1, Scheme 1) initially reported in 1971 to capturing UO_2,[66] can be synthesized in almost quantitative yields[67] and has two pockets that can coordinate to metal centres. Previously this ligand has been involved in the synthesis of homometallic[68–71] and heterometallic CCs.[72–75] .We recently employed this ligand in 3d/4f chemistry to synthesise a family of homogeneous efficient catalysts towards a domino reaction.[76] Interestingly, when H_2**L1** was employed in Ni(II) chemistry, a tetranuclear Ni_4 CC exhibiting ferromagnetic interactions at low temperatures was isolated. [71] With the interest of introducing carbonate anions into a system, there are three key methods; direct addition of carbonate or bicarbonate[14], atmospheric fixation of carbon dioxide[77] and in situ decomposition of ligands[78].

Having all these in mind, in this article we study the influence of the presence of Na cations and CO_3^{2-} anions on the nuclearity of the given chemical system Ni(II)/H_2L1 and we report two compounds formulated $[Ni^{II}_3Na(\mathbf{L1})_3(H\mathbf{L1})(MeOH)_2]$ (**1**) and $[Ni^{II}_6Na^{I}(\mathbf{L1})_5(CO_3)(MeO)(MeOH)_3(H_2O)_3]\cdot 4(MeOH)\ 2(H_2O)$ [**2** $4(MeOH)\ 2(H_2O)$]. Topological aspects and magnetic properties of these compounds are further discussed.

2. Experimental

Materials. Chemicals (reagent grade) were purchased from Sigma Aldrich and Alfa Aesar. All experiments were performed under aerobic conditions using materials and solvents as received.

Instrumentation. IR spectra of the samples were recorded over the range of 4000-650 cm^{-1} on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a UATR polarization accessory.

X-Ray Diffraction

Crystallography. Data for **1** and **2**·4(MeOH) were collected at the National Crystallography Service, University of Southampton[79] using a Rigaku Saturn 724+ area detector mounted at the window of an FR-E+ rotating anode generator with a Mo anode (λ=0.71075Å) under a flow of nitrogen gas at 150(2)K for **1** and 100(2) K for **2**·4(MeOH). Both structures were determined using Olex2,[80] solved using either Superflip[81] or SHELXT[82, 83] and refined with SHELXL-2014.[84] All non-H atoms were refined with anisotropic thermal parameters,

and H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. For **1**, attempts to model the lattice solvents (2MeOH) were unsuccessful despite multiple data collections. Therefore, the solvent mask function of Olex2[80] was employed to remove the contribution of the electron density associated with those molecules from the intensity data. Geometric/crystallographic calculations for all structures were performed using PLATON,[85] Olex2,[80] and WINGX[82] packages; graphics were prepared with Crystal Maker.[86] CCDC 1476870-1476871

Table 1. Crystallographic data for compounds **1** and **2**

	1	**2** 4(MeOH) 2(H_2O)
Empirical formula	$C_{59}H_{57}N_4NaNi_3O_{15}$	$C_{311}H_{353}N_{20}Na_4Ni_{24}O_{117}$
Formula weight	1261.20	7744.11
Temperature/K	150	100(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a/Å	13.5258(10)	12.4060(8)
b/Å	23.2626(16)	26.2551(18)
c/Å	18.9222(13)	27.7103(19)
α/°	90	113.152(2)
β/°	94.6777(8)	91.231(2)
γ/°	90	92.181(2)
Volume/$Å^3$	5934.0(7)	8286.4(10)
Z	4	1
$\rho_{calc}g/cm^3$	1.412	1.552
μ/mm^{-1}	1.018	1.426
F(000)	2616.0	4011.0
Crystal size/mm^3	0.19 × 0.08 × 0.05	0.22 × 0.03 × 0.01
Radiation	MoKα (λ = 0.71075)	MoKα (λ = 0.71075)
2Θ range for data collection/°	5.208 to 52.746	4.654 to 50.062
Index ranges	-17 ≤ h ≤ 17, -30 ≤ k ≤ 30, -24 ≤ l ≤ 24	-14 ≤ h ≤ 14, -28 ≤ k ≤ 31, -32 ≤ l ≤ 32
Reflections collected	64331	86087
Independent reflections	12109 [R_{int} = 0.0481, R_{sigma} = 0.0262]	28939 [R_{int} = 0.1207, R_{sigma} = 0.1309]
Data/restraints/parameters	12109/25/749	28939/1/2138
Goodness-of-fit on F^2	1.063	0.972
Final R indexes [I>=2σ (I)]	R_1 = 0.0596, wR_2 = 0.1391	R_1 = 0.0734, wR_2 = 0.1878
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1415	R_1 = 0.1249, wR_2 = 0.2167
Largest diff. peak/hole / e $Å^{-3}$	1.77/-0.72	1.82/-2.38

Magnetic studies. Magnetic susceptibility measurements were carried out on polycrystalline samples with a MPMS5 Quantum Design susceptometer working in the range 30-300 K under external

magnetic field of 0.3 T and under a field of 0.03T in the 30 – 2 K range to avoid saturation effects. Diamagnetic corrections were estimated from Pascal Tables. The quality of the fitting is parametrized as the factor $R = (\chi_M T_{exp} - \chi_M T_{calc})^2/(\chi_M T_{exp})^2$.

Synthesis of H_2L1

o-Vanillin (0.025mol, 3.35g) and 2-amino-phenol (0.025mol, 2.73g) were dissolved in MeOH (5mL). The suspension was refluxed for 1h, during which time a bright orange solid precipitated. After cooling to room temperature the solid was filtered off and washed with cold MeOH and Et_2O. The solid was dried in vacuo. Yield 99%. ^{1}H NMR (500 MHz, DMSO-d^6) δ 9.75 – 9.71 (m, 1H), 8.95 (s, 1H), 7.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.21 – 6.99 (m, 3H), 6.96 (dd, J = 8.1, 1.4 Hz, 1H), 6.91 – 6.81 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d^6) δ 162.01, 152.27, 151.42, 148.63, 134.95, 128.46, 124.26, 120.05, 119.96, 119.70, 118.37, 116.97, 115.71, 56.34, 40.62, 40.53, 40.45, 40.36, 40.28, 40.19, 40.11, 40.03, 39.95, 39.86, 39.69, 39.53.

Synthesis of 1

$Ni(ClO_4)_2.6H_2O$ (0.1mmol, 37mg), H_2**L1** (0.1mmol, 24mg) and Na_2CO_3 (0.1mmol, 10mg) were suspended in MeOH (20mL) and stirred for 1hour. The solution was filtered and the filtrate left for slow evaporation. After 14 days, small brown crystals of **1** were collected and washed with Et_2O. (Yield =45% calculated based on Ni(II)). IR (ν, cm^{-1}) = 3402, 3291, 1780, 1609, 1552, 1454, 1388, 1291, 1224, 1182, 1073, 1033, 964, 820, 733, 635. CHN $[Ni_3Na(C_{14}H_{11}NO_3)_3(C_{14}H_{12}NO_3)(CH_3OH)_2]$; observed C-56.63%; H-4.47%, N-4.43% (expected); C-56.76%; H-4.35%; N-4.56%

Synthesis of [2 4(MeOH) 2(H_2O)]

A similar synthetic procedure to **1** was followed, however after filtration the solution was placed in a vial which in turn was placed in a larger vial that contained a saturated aqueous solution of Na_2CO_3. A few drops of conc HCl was added to the saturated to solution and the vial was immediately sealed. After 5 days, large brown block-like crystals of compound [**2** 4(MeOH)] were collected. (Yield = 60% calculated based on Ni(II)). IR (ν, cm^{-1}) = 3288, 1604, 1552, 1451, 1388, 1294, 1229, 1182, 1075, 1037, 966, 818, 736, 637. CHN $[Ni_6Na(C_{14}H_{11}NO_3)_5(CO_3)(CH_3O)(CH_3OH)_3(H_2O)_3]$ (observed); C-49.51%; H-4.11%; N-3.79%; (expected) C-49.52%; H-4.21%; N-3.85%

3. Results and Discussion

Two Ni^{II}/Na^{II} CCs were synthesised. The aim to use of Na_2CO_3 as the base to introduce carbonate bridges to the system results in the presence of one Na^I in both CCs, while both compounds have different structures to the previously reported homometallic Ni^{II} CC with H_2L1.[69] In **1**, the use of Na_2CO_3 did not result in the introduction of carbonate bridging groups, however in **2** where the

reaction solution was exposed to a high CO_2 atmosphere during slow evaporation, a single CO_3^{2-} anion is observed. **1** and **2** are new additions to a large family of previously reported Ni^{II}/Na^{I} CCs.

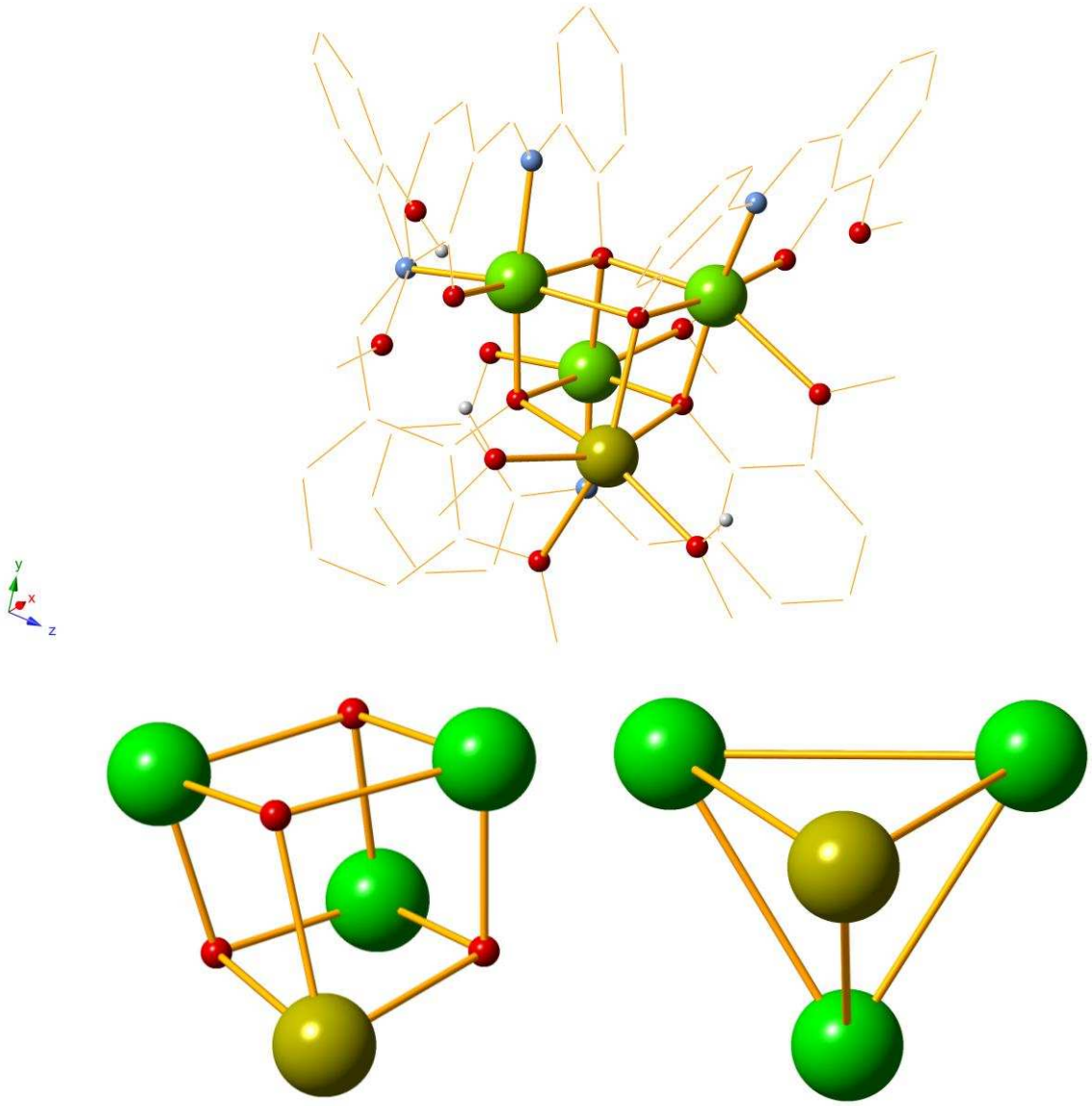
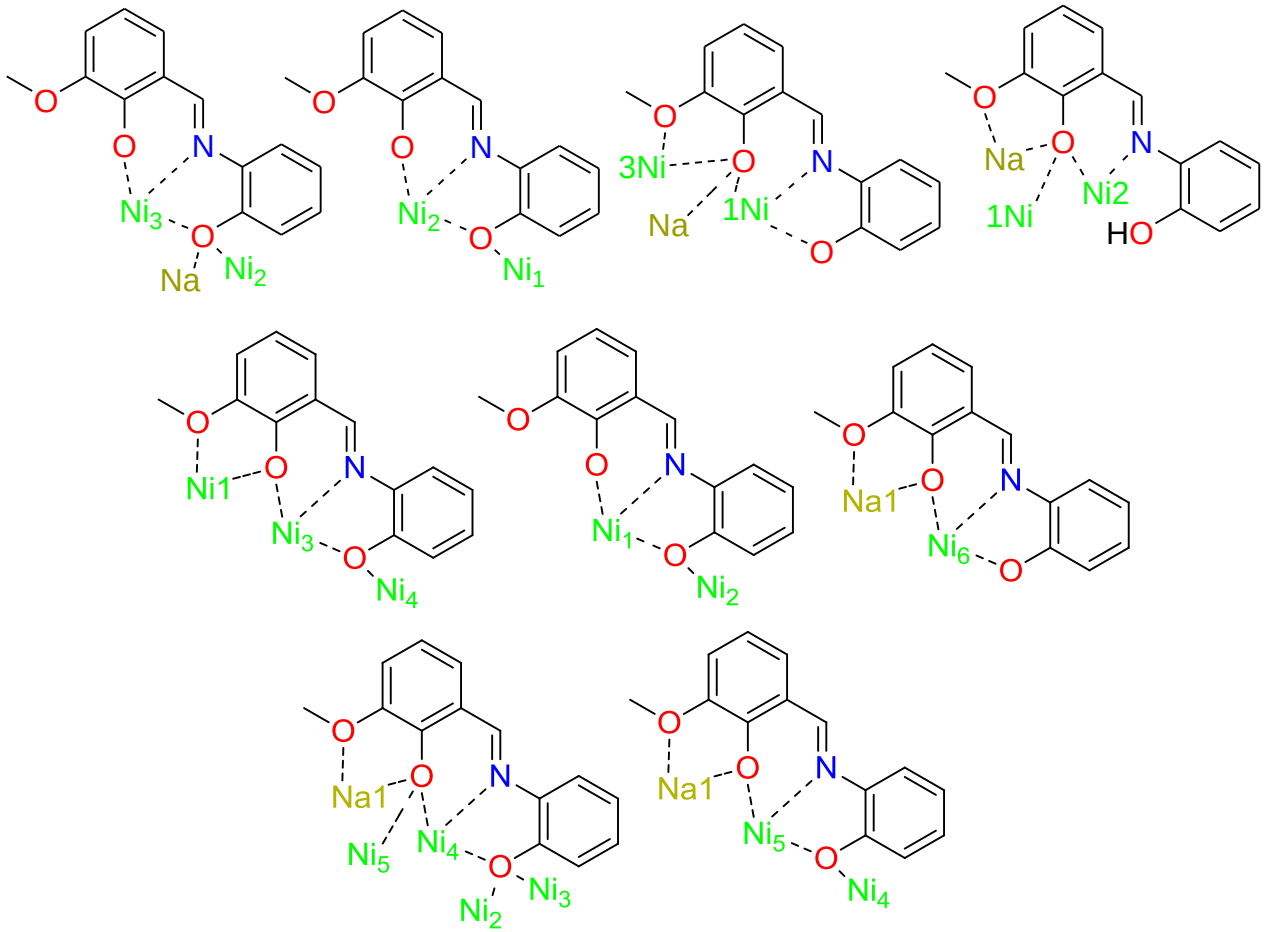


Figure 1. (upper) The crystal structure of compound **1**, (lower left) the main Ni_3Na core, (lower right) the **3M4-1** topology. Colour code Ni (green), Na (light yellow), O (red), N (blue), C (yellow)

1 crystallises in the monoclinic space group $P2_1/n$ and contains one molecule in the asymmetric unit cell. Compound **1** contains, three Ni^{II} ions, one Na^{I} ion, three doubly deprotonated (**L1**) ligands, one mono deprotonated (H**L1**$^-$) ligand, three co-ordinated CH_3OH solvent. Each Ni^{II} ion coordinate to six heteroatoms and displays a distorted octahedral geometry. There are three observed coordination modes for the doubly deprotonated ligands (**L1**) (Scheme 2), in each a Ni^{II} ion occupies the ONO pocket between the phenoxido and imido atoms. The singly protonated (H**L1**) ligand co-ordination mode (Scheme 2),[69, 71–74, 87–91] a Ni^{II} ion is observed occupying the OO pocket between the methoxido and phenoxide ligand atoms. Interestingly, **L1** demonstrates a

twisted-out of plane geometry between the two aromatic rings with a torsion angle of -100.679° along the C=C-N=C bond, whilst the **L1** Ligand aromatic rings are close to being in-plane with torsion angles between -166.840-174.23°. In addition to this both Ni^{II} and the Na^{I} are observed bridging from the phenoxido atoms. The Na^{I} ion displays a distorted octahedral geometry with, average Na-O bond distances ranging from 2.272-2.648A. Then three Ni^{II} ions all display distorted octahedral geometry with average Ni-O bind distances ranging from 1.981-2.343A. Four μ_3-$O_{phenoxo}$ donors are placed in the corners of the cube linking the four cations. Ni-O-Ni bridges form three faces of the cube with bond angles of 97.0(1)º/97.7(1)º, 97.18(9)º/99.87(9)º and 93.38(9)º/102.7(1)º.

According to a nomenclature, developed by some of us,[92] the decorated core of this compound is assigned **3M4-1** (Figure 1). An extended literature survey reveals only three previously reported complexes with Ni_3Na core topologies, each of which are synthesised from similar Schiff base ligands and coordination pockets to H_2**L1**.[93, 94] The most recently reported of these Zhang et al[93] shares the same **3M4-1** topology as **1**, making **1** the second example of a Ni^{II}_3/Na^{I} cubane.



Scheme 2. The coordination modes of the organic ligand H_2**L1** seen in **1** (upper) and **2** (middle and lower).

Table 2. Selected bond distances and angles for compound 1.

Ni1	O2	1.972(2)	Ni3	N2	1.979(3)	
Ni1	O3	1.989(3)	Na1	O2	2.646(3)	
Ni1	O9	2.095(2)	Na1	O6	2.272(3)	
Ni1	O11	2.188(3)	Na1	O10	2.334(4)	
Ni1	O48	2.144(3)	Na1	O11	2.333(3)	
Ni1	N1	2.011(3)	Na1	O15	2.329(3)	
Ni2	Na1	3.2461(18)	Na1	O25	2.295(5)	
Ni2	O8	1.994(2)	Ni1	O11	Na1	108.68(11)
Ni2	O9	2.089(2)	Ni2	O11	Ni1	97.02(11)
Ni2	O6	2.275(2)	Ni2	O11	Na1	96.31(10)
Ni2	O11	2.015(2)	Ni1	O2	Ni3	102.69(12)
Ni2	N4	2.131(3)	Ni1	O2	Na1	104.49(11)
Ni2	N3	1.979(3)	Ni3	O2	Na1	93.47(10)
Ni3	Na1	3.4000(17)	Ni1	O9	Ni3	93.38(9)
Ni3	O1	2.340(2)	Ni2	O9	Ni1	97.68(10)
Ni3	O2	1.980(3)	Ni2	O9	Ni3	99.87(9)
Ni3	O9	2.146(2)	Ni3	O6	Ni2	97.18(9)
Ni3	O5	1.982(3)	Ni3	O6	Na1	103.91(10)
Ni3	O6	2.041(2)	Na1	O6	Ni2	91.09(9)

Compound **2** crystallises in the triclinic P-1 space group and contains two molecules in the asymmetric unit. The molecule of **2** contains six Ni^{II} ions, one Na^{I} ion, five doubly deprotonated **L1** ligands, one bridging (μ_5-CO_3), one deprotonated MeOH solvent molecule with three CH_3OH and three H_2O molecules which fulfil the co-ordination geometry of the metal ions.

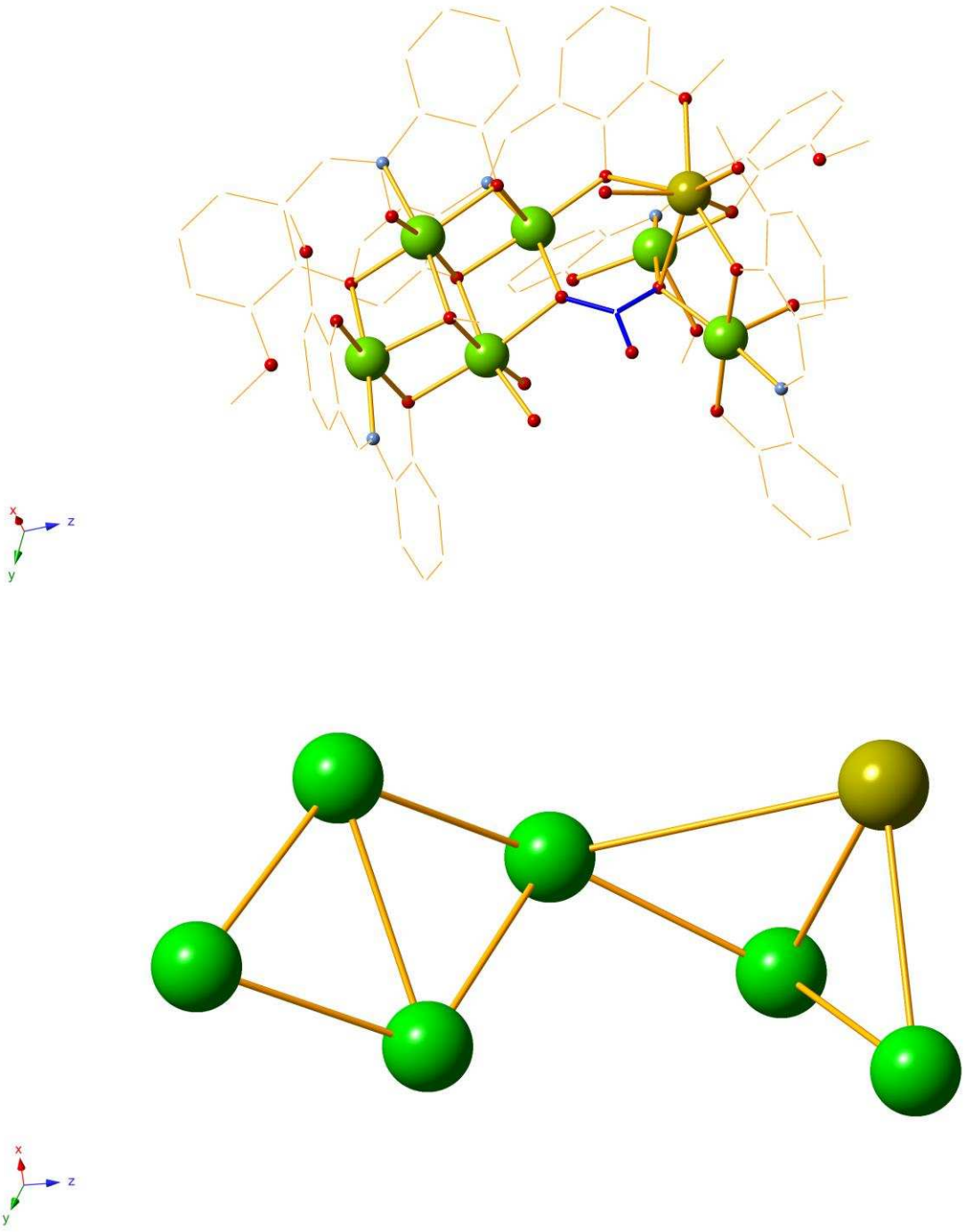
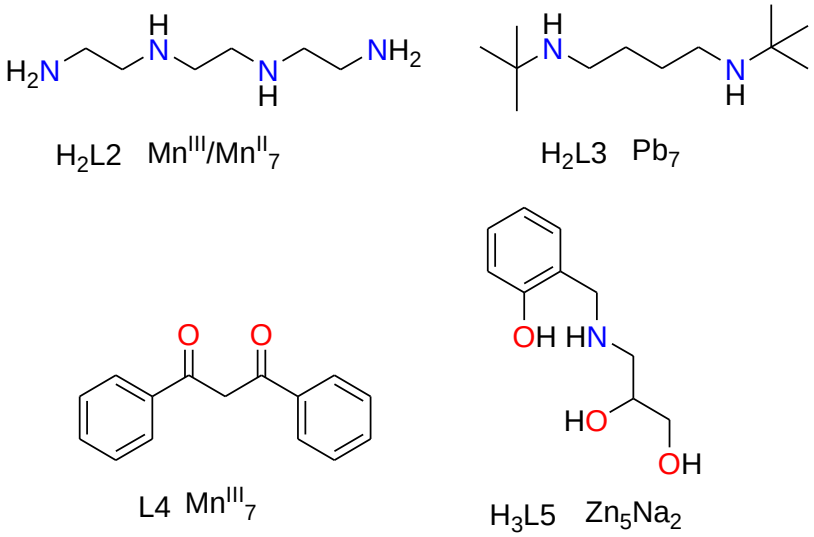


Figure 2. (upper) The crystal structure of compound **2**. Lattice molecules and H-atoms are omitted for clarity. Colour code Ni (green), Na (light yellow), O (red), N (blue), C (yellow). (lower) The **2,3,4M7-1** topology of compound **2**.

All six Ni^{II} ions have a distorted octahedral geometry. The **L1** demonstrates four different bridging modes (Scheme 2) with Ni^{II} ions observed occupying the (ONO) and (OO) pocket as well as bridging from the phenoxido, methoxido and imine groups. The Na^{II} ion is seven coordinated and the coordination geometry can best be described as a capped trigonal prism determined by SHAPE software. The Na^{I} ion coordinates to the (OO) pocket between the methoxide and phenoxido atoms

of three ligands with the seventh position fulfilled by a H_2O molecule. The CO_3^{2-} entity bridges Ni2, Ni4, Ni5 and Ni6 through a (μ_5-CO_3) ion. Na-O bond distances range from 2.282-2.625A. The Ni – O and Ni – N distances vary between 1.983(6) and 2.321(4)Å, while the Ni – O – Ni angles mediated by the $O_{phenoxo}$ donors vary from 88.88(17) and 101.8(2)°, those mediated by the μ_3-OMe bridge, that links Ni1, Ni2 and Ni3, exhibit bond angles ranging between 95.74(19)-100.2(2)º and Ni5-O22-Ni6, mediated by one $O_{carbonate}$ atom reach 130.4(2)º.



Scheme 3. Protonated forms of the organic ligands used for the synthesis of 3d and 3d/Na CCs possessing the **2,3,4M7-1** topology.

Adopting our topological approach, the core of compound **2** can be enumerated as **2,3,4M7-1**.[92] The **2,3,4M7-1** core topology can be viewed as two lozenges fused with a shared apex vertices (Figure 2 lower), this can be otherwise described as a "butterfly" motif, where the shared vertices are the body and the protruding lozenges the "wings". The first reported compound of this topology was a mixed valence Mn^{II}/Mn^{III} complex in 1991.[95]. This was subsequently followed by a number of homometallic CCs, including Mn^{III},[96] and Pb^{II},[97]. The first heterometallic complex of this topology was reported in 2012 with the core topology of Zn_5Na_2[98] with the ((2,3-dihydroxypropylamino)methyl)phenol ligand (Scheme 3 H_3L5). The metal ion positions of this core topology differ to the reported compound **2**. The Na^I ions occupy the two apex vertices of the two fused lozenges with all other positions occupied by the 3d Zn^{II} ions. In both examples the fused vertice is occupied by a 3d ion (Ni^{II}/Zn^{II}). Metal ion geometries widely differ in both complexes, with Na^I ions possessing severely distorted octahedral geometry and Zn^{II} ions tetrahedral. Both of these complexes are formed from Schiff base ligands incorporating the 2-hydroxy-benzaldehyde moiety, which provides a similar co-ordination environment, with further bridging attributed to the third hydroxyl group in H_3L5. To the best of our knowledge **2** is the first example of an Ni^{II}/Na^I CC exhibiting the **2,3,4M7-1** topology. Moreover, ignoring the existence of the Na ion, then the motif of

the hexanuclear Ni_6 unit can be enumerated as **1,2,2,3,3M6-1** (Figure S3), which has been reported only once before in Zinc chemistry.[99]

Table 3. Selected bond distances and angles for compound **2**.

Ni1	N1	1.987(6)	Ni7	O30	1.961(5)	Ni3	O5	Ni1	101.84(19)
Ni1	O3	1.990(5)	Ni7	O27	1.976(5)	Ni2	O6	Ni1	96.90(19)
Ni1	O5	1.998(4)	Ni7	N6	1.985(6)	Ni2	O16	Ni3	100.20(18)
Ni1	O6	2.059(5)	Ni7	O28	2.046(5)	Ni4	O51	Ni2	101.50(19)
Ni1	O16	2.076(4)	Ni7	O41	2.099(5)	Ni4	O51	Ni3	95.74(19)
Ni1	O4	2.321(4)	Ni7	O29	2.297(5)	Ni2	O51	Ni3	95.13(17)
Ni2	O16	2.017(5)	Ni8	O41	2.016(5)	Ni5	O11	Na1	88.28(18)
Ni2	O6	2.053(5)	Ni8	O43	2.059(5)	Ni5	O12	Ni4	89.88(17)
Ni2	O17	2.069(5)	Ni8	O28	2.059(5)	Ni4	O20	Ni2	99.50(18)
Ni2	O18	2.071(5)	Ni8	O44	2.071(5)	Ni5	O22	Ni6	130.4(2)
Ni2	O51	2.086(4)	Ni8	O34	2.092(5)	Ni5	O22	Na1	91.49(18)
Ni2	O20	2.133(4)	Ni8	O45	2.135(4)	Ni6	O22	Na1	95.31(18)
Ni3	O5	1.954(4)	Ni9	O30	1.941(5)	Ni6	O14	Na1	103.8(2)
Ni3	O8	2.040(5)	Ni9	N7	1.997(6)	Ni4	O52	Ni5	90.12(19)
Ni3	N2	2.040(6)	Ni9	O54	2.031(5)	Ni4	O52	Na1	116.1(2)
Ni3	O16	2.062(5)	Ni9	O41	2.061(5)	Ni5	O52	Na1	81.76(16)
Ni3	O2	2.075(6)	Ni9	O42	2.088(5)	Ni7	O28	Ni8	97.7(2)
Ni3	O51	2.153(5)	Ni9	O34	2.178(5)	Ni9	O30	Ni7	103.6(2)
Ni4	N3	1.993(6)	Ni10	O33	1.993(5)	Ni10	O34	Ni8	101.92(19)
Ni4	O52	2.017(5)	Ni10	N8	2.001(5)	Ni10	O33	Na2	116.2(2)
Ni4	O51	2.040(5)	Ni10	O34	2.020(4)	Ni11	O33	Na2	83.77(17)
Ni4	O20	2.053(4)	Ni10	O45	2.049(4)	Ni10	O34	Ni9	93.77(18)
Ni4	O8	2.153(5)	Ni10	O54	2.143(5)	Ni8	O34	Ni9	94.16(17)
Ni4	O12	2.213(5)	Ni10	O37	2.234(5)	Ni11	O36	Na2	85.61(18)
Ni5	N4	1.987(5)	Ni11	N9	1.982(5)	Ni11	O37	Ni10	89.16(17)
Ni5	O11	1.989(4)	Ni11	O36	1.997(5)	Ni8	O41	Ni9	100.21(19)
Ni5	O22	2.011(4)	Ni11	O46	2.020(4)	Ni12	O39	Na2	103.0(2)
Ni5	O12	2.031(4)	Ni11	O37	2.057(4)	Ni8	O41	Ni7	97.32(19)
Ni5	O25	2.145(6)	Ni11	O50	2.122(5)	Ni9	O41	Ni7	94.99(19)
Ni5	O52	2.218(5)	Ni11	O33	2.212(5)	Ni11	O46	Na2	92.85(19)
Ni6	O14	1.957(5)	Ni12	O39	1.967(5)	Ni12	O46	Na2	95.00(18)
Ni6	N5	1.983(6)	Ni12	N10	1.972(6)	Ni9	O54	Ni10	94.49(19)
Ni6	O15	2.043(5)	Ni12	O40	2.034(5)	Ni10	O45	Ni8	99.49(18)
Ni6	O22	2.067(4)	Ni12	O46	2.057(5)	Ni11	O46	Ni12	129.5(2)
Ni6	O23	2.086(5)	Ni12	O49	2.096(5)				
Ni6	O21	2.229(5)	Ni12	O47	2.244(5)				
Na1	O14	2.282(5)	Na2	O39	2.278(6)				
Na1	O7	2.342(5)	Na2	O90	2.306(7)				
Na1	O24	2.353(7)	Na2	O32	2.318(6)				
Na1	O22	2.442(5)	Na2	O46	2.444(6)				
Na1	O11	2.572(6)	Na2	O33	2.629(5)				
Na1	O13	2.615(5)	Na2	O38	2.659(5)				
Na1	O52	2.651(5)	Na2	O36	2.718(6)				

4. Magnetic Studies

The $\chi_M T$ value at room temperature for compound **1** is 3.97 cm^3Kmol^{-1}, increase on cooling to a maximum value of 4.50 cm^3Kmol^{-1} at 13 K, prior to decrease at low temperature, indicating a dominant weak ferromagnetic interaction. Fit of the experimental data was performed with PHI[100] program and applying the Hamiltonian:

$$H = -2J_1(S_1 \cdot S_2 + S_1 \cdot S_3) - 2J_2(S_2 \cdot S_3)$$

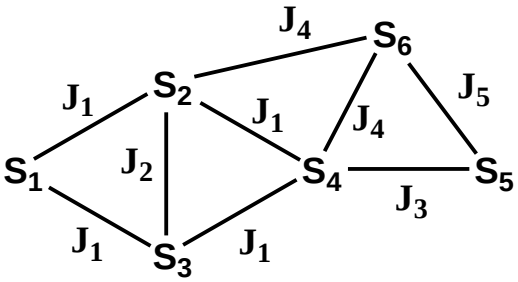
including a D_{ion} parameter. Considering the D_{ion} parameter an excellent fit of the experimental data was obtained for the parameters J_1 = 3.6 cm^{-1}, J_2 = -2.3 cm^{-1}, D = 1.2 cm^{-1}, g = 2.26 and $R = 4.2 \cdot 10^{-5}$ but this was not the case when the isotropic Hamiltonian were applied. The shape of the $\chi_M T$ plot corresponds to a weak ferromagnetic coupling with a strong decrease at low temperature due to combination of the AF component and the ZFS of the same order of magnitude than J.

The $\chi_M T$ value at room temperature for **2** is 7.1 cm^3Kmol^{-1} at room temperature and on cooling increases slight up to a rounded maximum of 7.34 cm^3Kmol^{-1} at 45 K. Below this temperature the $\chi_M T$ value decreases down to 5.94 cm^3Kmol^{-1} at 2 K. From the structural data, compound **2** consists of a Ni_4 butterfly subunit linked by means of different kind of bridges to two additional Ni^{II} cations and thus, the corresponding Hamiltonian to analyse the experimental data must be:

$$H = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_4 + S_3 \cdot S_4) - J_2(S_2 \cdot S_3) - J_3(S_4 \cdot S_5) - J_4(S_2 \cdot S_6 + S_4 \cdot S_6) - J_5(S_5 \cdot S_6)$$

This expression is clearly overparametrized and different solutions can be obtained assuming all constants or simplifying the Hamiltonian (in all cases R factor in the 10^{-5}-10^{-6} range). This feature is a consequence of the topology of that complex: the butterfly subunit can give any local spin between S = 0 and S = 4 as function of the J_1 and J_2 values and in addition the two additional Ni^{II} cations forms triangular subunits in which there are competitive interactions and thus, only a qualitative analysis can be made.

It is well established that the FM/AF border for Ni-O-Ni bridges is placed around 96º for hydroxo bridges and values slightly larger for alkoxo or phenoxo ones. The most of the Ni-O-Ni bond angles in compound **2** lies around this border and thus, only weak ferro or antiferromagnetic interactions can be expected. In contrast, the very large Ni5-O22-Ni6 bond angle mediated by one of the O-donors of the carbonate ligand must give a clear AF interaction. In good agreement, all obtained fits gave a large dispersion of values for J_1-J_4 but in all cases J_5 gave a value around -7 cm^{-1} (scheme 4). In light of this data we must assume that two S = 1 local spins are cancelled whereas the remainder four spins are related by weak interactions.



Scheme 4. A schematic representation of the exchange couplings seen in compound 2.

The presence of competitive interactions is reinforced by magnetization experiments. The unsaturated value under a field of 5 T is 6.25 Nμβ and can be reasonably fitted as an isolated S = 3 spin with D = 0.89 cm^{-1} and g = 2.14.

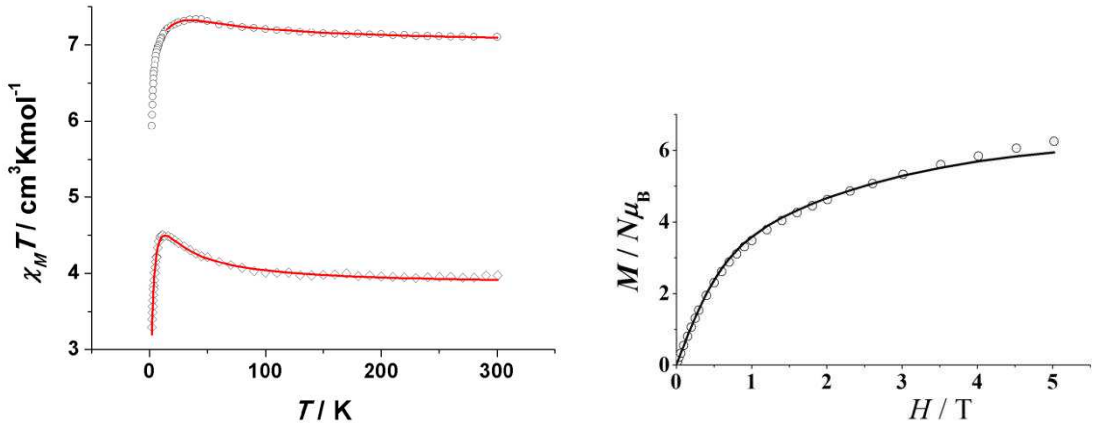


Figure 3. (left) χ_MT vs. T plots for the complexes **2** (circles) and **1** (diamonds). Solid lines show the fit of the experimental data for **1** and one of the fits obtained for **2**. (right) The magnetization plot for compound **2**.

5. Conclusions

Our synthetic strategy to introduce Na^I and carbonate, as co-ligand, along with H_2L1 in Ni chemistry, resulted in two new Ni/Na compounds possessing a rare (for **1**) and an unseen (for **2**) topology. Magnetic studies reveal the presence of weak ferromagnetic interactions at low temperature for both compounds. Assumptions for the structural relationship of **1** and **2** can be attempted, but more synthetic studies are required to support its. Our future studies will be focused in two different directions: a) to extend the systematic synthetic study by varying metal ligand ratios and co-ligands aiming to achieve higher nuclearity CCs and b) to further develop our topological approach[101] by incorporating all centers as nodes.

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